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Process Optimization for Biodiesel Production from Waste Frying Oil over Montmorillonite Clay K-30

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Abstract

Biodiesel that mostly comes from pure renewable resources provide an alternative fuel option for future because of limited fossil fuel resources as well as environmental concerns. The transesterification of non-edible oils for biodiesel production is one of the promising process for biodiesel production to overcome this future crises of energy. The utilization of waste frying oil into biodiesel have great worth for economization of biodiesel cost as well as the conversion of waste into value added product with environmental protection. The purpose of the present work is to optimize the process of biodiesel production over a heterogeneous clay based catalyst. Particularly, the transesterification of waste frying palm oil with methanol was studied in the presence of montmorillonite clay K-30 as solid base catalyst that have both of acid and basic nature. The observed date was then optimized with the help of Design of Experiments software. The Response Surface Methodology (RSM) based on four-variable central composite design (CCD) with α (alpha) = 2 was used for this purpose. The transesterification process variables were reaction temperature, x_1 (40-140°C), reaction period, x_2 (60-300 min), methanol/oil ratio, x_3 (6:1- 18:1mol/ mol) and amount of catalyst, x_4 (1-5% wt). The results showed that waste frying oil is a good feedstock for biodiesel production and high yield of 78.4% was obtained during optimization of this biodiesel process that was noted after 180 min at temperature 90℃, with a 12:1molar ratio of methanol to waste frying oil and using 3%wt of montmorillonite clay K-30 catalyst.

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1. Introduction

Energy demand and its resources are increasing day by day due to the rapid outgrowth of population and urbanization. Currently, fuel crisis has globally flounced the economy in every region, especially the oil consuming countries due to its rapidly decreasing available global stock. In view of this serious situation, biodiesel which comes from 100% renewable resources provides an alternative fuel option for future. This green fuel has the same characteristics as conventional diesel (Cetane number, viscosity, cloud point and flash point) which make it one of the most favorable among new energy resources [1,2]. Biodiesel still has not been commercialized globally due to its high production cost. The major restricting factor in the development of biodiesel is the feedstock for its formation. According to previous researcher [3,4], the most common commercial process for biodiesel production is homogeneous alkali-catalyzed transesterification in the presence of methanol using refined edible or non-edible oils as raw materials. In Malaysia, palm oil is effectively use as a feedstock for the production of biodiesel due to abundant cultivation of palm trees. However, this type of edible oil has considerable amount of free fatty acids (FFAs) which required a proper choice of catalyst for transesterification during biodiesel formation process.

The selection of catalyst for such process is an art due to requirement of its high effectiveness for biodiesel yield as well as separation from main product. Most of homogenous catalysts are active for biodiesel formation reactions but sensitive to water and FFAs present in feedstock which can form unwanted soap as a by-product. This by-product makes the final product separation difficult and also reduces the activity of the catalyst. A massive environmental unfriendly water washing process is required for separation of such type of soap bye-product as well as removal of homogenous catalyst from final product. Heterogeneous catalyst can overcome these problems as compared to homogeneous one for both commercial and environmental point of view. So far, a variety of different heterogamous catalysts for biodiesel production have been investigated, including zeolite [5,6], alkaline earth oxides, ion-exchange resin [7], hydrotalcites, inorganic-oxide solid acid, supported alkaline or alkaline earth metals and supported noble-metal oxide [8, 9]. Most of these catalysts are commonly found hydrophilic and their activity decreases due to the presence of water which produces during FFA esterification. Moreover, they have high cost, bad structure stability and low density of effective acid sites. Therefore, such drawbacks have limited these catalysts for their practical use in biodiesel production.

Experiments have been carried out by using clay based solid catalyst in biodiesel production. Recently some researchers have utilized clay as heterogamous catalyst to make biodiesel production more economical and ecofriendly. It is reported that the catalyst prepared from clay could be reused without much loss in activity and can be separated easily from main product. The previous researchers used clay catalyst for production of biodiesel from different feedstock [10]. However, very little work is reported for using clay as solid catalyst. Therefore the present study was done with objective to produce biodiesel from palm oil using montmorillonite clay K-30 as heterogeneous clay catalyst. The optimization of biodiesel process was achieved with a statistical design of experiment using response surface methodology (RSM) to accumulate and analyze information on the effect of four process variables on the yield of transesterification in a rapid and efficient manner using a minimum number of experiments. The utilization of inexpensive waste frying oil as well as clay based catalyst, surely minimize the cost of biodiesel production. This also helps to exploring of an economic and environmental friendly process for sustainable energy.

2. Experimental

2.1. Materials

Waste frying oil was collected from local Restaurant in Bandar Sri Iskandar, Perak, Malaysia whereas methanol from Sigma-Aldrich, Malaysia. Methyl heptadecanoate (used as internal standard) and standard references for FAME analysis; methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were obtained from Fluka Chemie, Germany. The catalyst, montmorillonite K-30 (in powder form), also purchased from Sigma-Aldrich, Malaysia. These materials from different companies were used as received without any pretreatment.

2.2. Design of experiments

The experimental design selected for this study is a Central Composite Design (CCD) that helps in investigating linear, quadratic, cubic and cross-product effects of the four transesterification process variables (independent) on the yield of biodiesel (FAME) response. The four transesterification process variables studied are reaction temperature, reaction period, ratio of oil to methanol and amount of catalyst. Tab. 2 lists the range and levels of the four independent variables studied. The CCD comprises a two-level small factorial design ($½ \times 2^4 = 8$), eight axial or star points and five centre points. The value of α (alpha) for this CCD is fixed at 2. The level of the process variables selected for this study are shown in Table 1.

Table 1. Levels of the process variables selected for this study

		Level				
Variables	Unit	-2	-1	0	+1	+2
Reaction temperature	°C	40	65	90	115	140
Reaction period	Min	60	120	180	240	300
Ratio oil/methanol	Ratio	1:6	1:9	1:12	1:15	1:18
Amount of catalyst	Wt %	1.0	2.0	3.0	4.0	5.0

Each response of the transesterification process was used to develop a mathematical model that correlates the yield of biodiesel production to the transesterification process variables studied through first order, second order and interaction terms, according to the following second order polynomial equation,

$$Y = b_o + \sum_{j=1}^{4} b_j x_j + \sum_{ij=1}^{4} b_{ij} x_i x_j + \sum_{j=1}^{4} b_{jj} x_j^2 \quad (1)$$

Where Y is the predicted yield of palm oil FAME, mol mol^{-1}, x_i and x_j represent the variables or parameters, b_o is the offset term, b_j is the linear effect, b_{ij} is the first order interaction effect and b_{jj} is the squared effect.

2.3. Activity study

Transesterification reactions were carried out in a batch reactor with a magnetic stirrer. Mixture of palm oil, catalyst and methanol was charged into the reactor. The mixing intensity of the magnetic stirrer was set at 190-200 rpm. The reaction temperature, duration, ratio of oil/methanol and amount of catalyst (montmorillonite clay K-30) were set according to the values proposed in the DOE shown in Table 3. The experiments were carried out in a random manner to minimize the effects of the uncontrolled factors. The excess methanol from the samples was removed using rotary evaporator. The upper layer of the sample was separated from the bottom layer and immediately quenched with n-hexane (dilution) prior to analysis of FAME content.

2.4. Analysis

The analysis of synthesised biodiesel samples in the form of FAME contents were carried out using Gas Chromatography (GC) by means of Inert Cap WAX capillary column (30 mm x 0.25 mm, I.D. 0.25 µm). Helium was used as the carrier gas. Oven temperature at 120°C was initially hold for 1 minute and then increased to 220°C (hold 15 minute) at a rate of 4°C min^{-1}. The temperatures of the injector and detector were set at 220°C and 250°C respectively. A quantity of 1 µl from each sample was injected into the column.

3. Results & Discussion

The activity of prepared catalyst for biodiesel production under transesterification processes is shown in Table 2. Based on these results obtained from this table, the highest biodiesel yield 78.40 % was achieved at a reaction temperature of 90°C, reaction period of 180 min, oil/methanol ratio of 1:12 and catalyst amount of 3 wt% respectively. The lowest conversion 34.58 % was obtained at a reaction temperature of 40°C, reaction period of 180 min, oil/methanol ratio of 1:12 and catalyst amount of 3 % respectively.

Table 2: The DOE experimental matrix and results for the transesterification processes

Run	Reaction Time	Reaction Temp	Catalyst Amount	Ratio O/M	Yield
	min	°C	wt %	mol/mol	%
1	240	115	2	1/15	56.84
2	240	65	4	1/15	51.54
3	240	65	2	1/09	47.93
4	240	115	2	1/09	62.24
5	180	90	2	1/12	74.96
6	120	115	4	1/09	72.57
7	300	90	3	1/12	71.25
8	240	65	4	1/09	75.42
9	240	90	3	1/12	76.15
10	120	65	4	1/09	69.54
11	240	115	4	1/09	70.65
12	120	115	2	1/15	71.54
13	180	90	3	1/12	73.85
14	180	140	3	1/12	60.45
15	120	65	4	1/15	58.68
16	180	90	3	1/06	64.35
17	180	90	3	1/12	61.85
18	120	65	2	1/15	76.95
19	120	65	2	1/09	56.25
20	240	65	2	1/15	53.56
21	240	115	4	1/15	62.52
22	180	90	3	1/18	48.52
23	180	90	3	1/12	54.62
24	180	40	3	1/12	34.58
25	120	115	4	1/15	75.85
26	60	90	3	1/12	76.45
27	120	115	2	1/09	67.54
28	180	90	5	1/12	76.95
29	180	90	3	1/12	78.40
30	180	90	1	1/12	41.54

A line of unit slope, i.e. the line of perfect fit with points corresponding to zero error between experimental and predicted values using the model equation is shown in Figure 1. This plot therefore visualizes the performance of the model in an obvious way. The results in Fig. 1 demonstrated that the regression model equation provided a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the four transesterification process variables to the yield of biodiesel via waste frying oil.

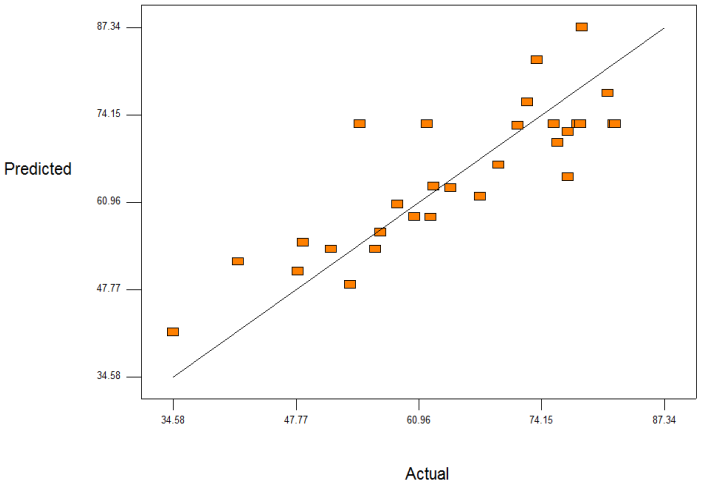

Figure 1. Predicted versus experimental yield of biodiesel production

Statistical analysis obtained from the analysis of variance (ANOVA) for the response surface reduced quadratic model is shown in Table 3. The value of "P > F" for the models is less than 0.05 to indicate that it is significant and desirable as it indicates that the terms in the model that have a significant effect on the response. The value of P > 0.05 indicates that there is only a small chance that a "model F-value" this large could occur due to noise in the experiment. Generally P-values lower than 0.01 indicates that the model is considered to be statistically significant at the 99% confidence level. The Model F-value of 2.63 implies the model is significant. There is only a 3.68% chance that a "Model F-Value" this large could occur due to noise. The "Lack of Fit F-value" of 0.52 implies the Lack of Fit is not significant relative to the pure error. There is 82.13% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good to fit the model.

Table 3: ANOVA analysis for quadratic model

Source	SS	DF	MS	F Value	Prob > F	
Model	3384.24	14.00	241.71	2.63	< 0.0368	Significant
Residual	1379.79	15.00	91.99			
Lack of Fit	704.93	10.00	70.49	0.52	0.8213	Not significant
Pure Error	674.86	5.00	134.97			
Cor Total	4764.04	29.00				
Std. Dev.	9.59		R-Squared			0.7104
Mean	65.18		Adj R-Squared			0.4401
C.V.	14.71		Pred R-Squared			-0.0563
PRESS	5032.21		Adeq Precision			6.786

Figure 2 shows the yield of biodiesel production with varying different variables in two dimensional (2D) plot. The change in yield of biodiesel production with varying reaction time at 2% and 4% catalyst is shown in Figure 2(a). The other two process variables; reaction temperature and ratio of oil to methanol were kept constant at 90^{o}C and 1: 12 respectively. As shown in this figure, at shorter reaction period, 2% catalyst showed a significant lower

biodiesel yield compared to that of 4% catalyst. This efficiency was continuously decreasing for both catalyst percentages with increasing reaction time. However, the yield by 4% catalyst less decreased as compared to that of 4% catalyst after 240 min of reaction. The both oil/methanol ratios with increasing conversion of palm oil to biodiesel with increasing reaction temperature as shown in Figure 2(b). Apart from that, higher ratio of oil/methanol, 1:15, gives lower conversion whereas lower ratio of oil/methanol, 1:9, gives higher production of biodiesel. It may possible that the equilibrium of the reaction slow down with the additions of more methanol that may cause to effect on heat of reaction when more methanol is used in the reaction. The variation in reaction time at different reaction temperature 65 and 115^{o}C is shown in Figure 2(c). The other two process variables; catalyst amount and ratio of oil to methanol were kept constant at 3 % and 1: 12 respectively. In this figure it is clear that throughout the reaction period, reaction at 65^{o}C showed a significant lower biodiesel yield compared to that of 115^{o}C.

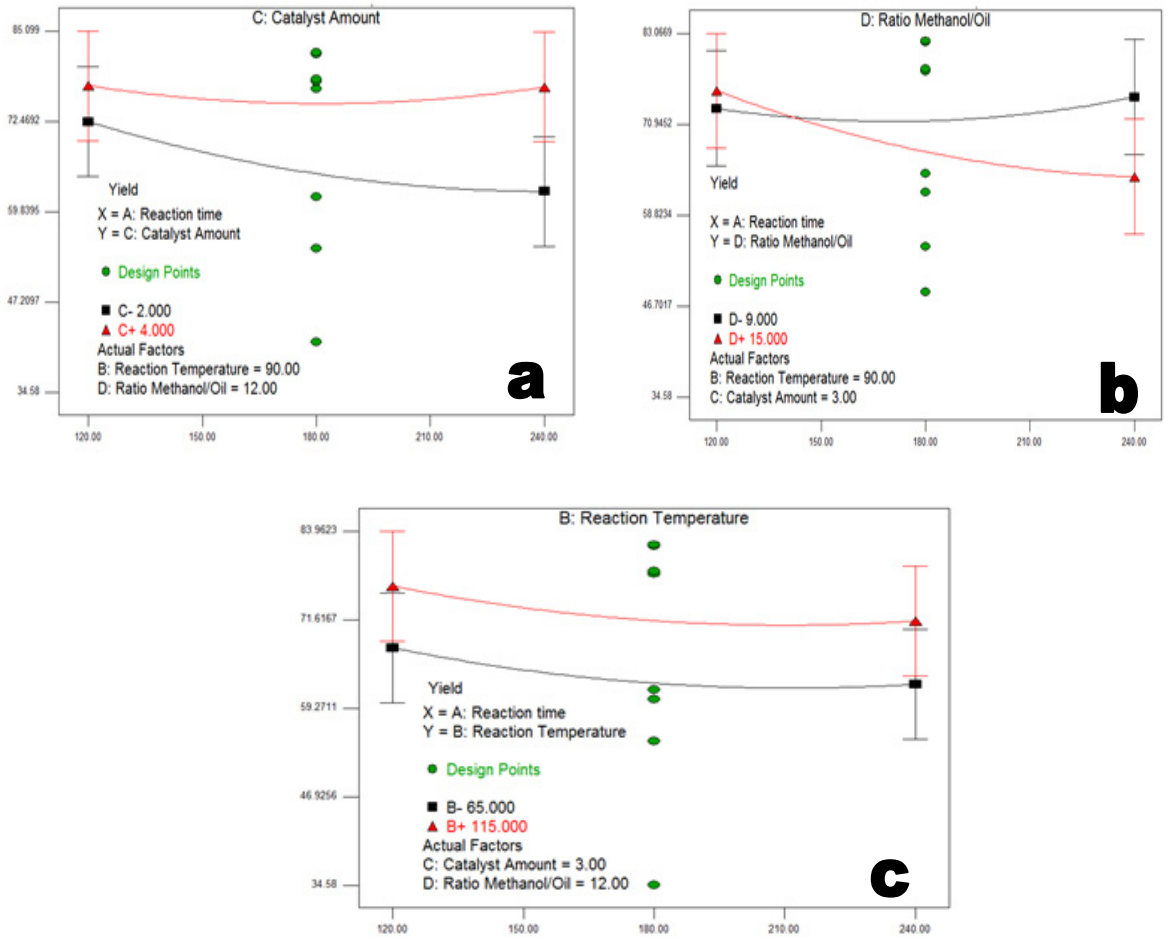

Figure 2: Two dimensional Interaction between a) time and catalyst amount b) temperature and methanol/oil ratio c) reaction temperature and time for biodiesel yield

The three dimensional (3D) and contour plots for the interaction between the reaction temperature and reaction time towards diglycerol yield are shown in Figure 3. It is clear from this 3D plot that when the reaction was carried out at a lower temperature of 65ºC, the yield was found to be less than 60 %. However, the yield increased with increasing reaction temperature to its central level (90ºC) while it start to decrease as the temperature was further increased to its high level (115ºC). This trend was found to change with changing reaction time (120 to 240 min). At

the start of the reaction with low temperature value, the yield was found to be low and the trend was found to be quite different with increasing temperature. However, it was more pronounced at longer reaction time. At lower temperature, less energy is supplied to the reactions whereas at higher temperature, more energy is supplied to the reactions. Higher ratio could means adequate energy is supplied to activate all the total sites of the catalyst and lower ratio means otherwise. At higher temperature, the total energy supplied to catalyst is more than adequate to activate all the active sites, the limitations of activity could probably come only from the amount of active sites of the catalyst itself. It is clear from this figure that the conversion of oil to biodiesel was found to be slightly lower at 240 min of reaction period as compared to 120 min when the catalyst amount was used 3 %. This may suggest the real interactions between the supplied energy (heat) and the active site on the catalyst itself. The active sites on the catalysts may require a certain amount of energy to be activated. At lower temperature, smaller amount may reach the activation energy but at higher temperature may this stage achieve earlier. In other words, the total energy required to activate the whole active sites on the 3% catalyst is much smaller for 65^{o}C than those for 115^{o}C. At lower temperature, less energy is supplied to the reactions whereas at higher temperature, more energy is supplied to the reactions [11]. Thus, temperature at 115^{o}C may just be enough to activate the whole active site on the 3% catalyst. Thus, only the perception that given amount of catalyst will results in higher conversion applies when the reaction temperature is sufficient high to activate all the active sites of the catalyst.

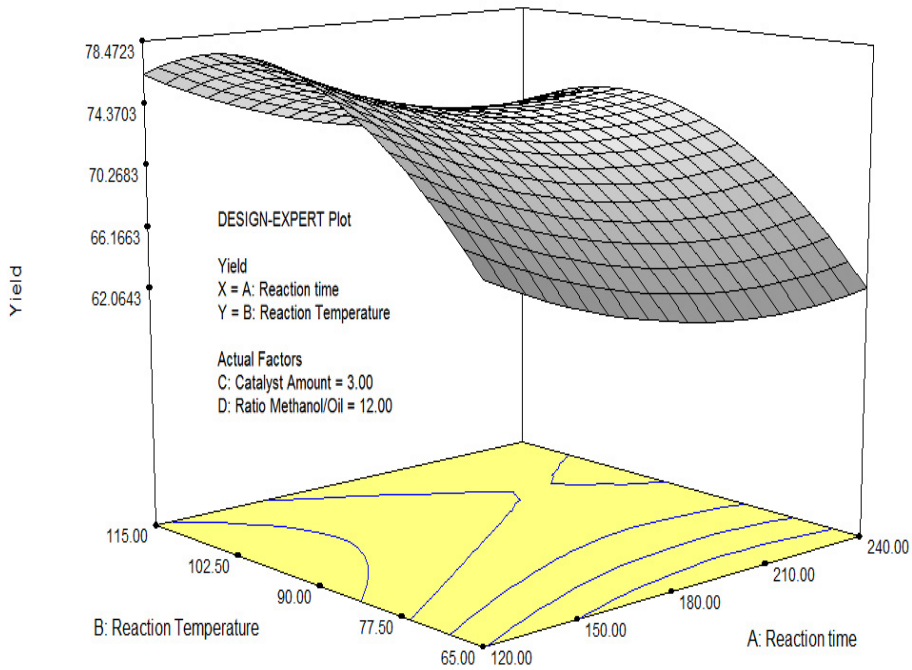

Figure 3: Three dimensional and contour plots for the effect of reaction time and temperature on biodiesel (FAME) yield %

4. Conclusion

Cost of biodiesel can be reduced by using waste frying oil as feed stock. The production of biodiesel from waste frying oils is feasible by transesterification process using montmorillonite clay K-30 as a catalyst. RSM was used to optimize the process variables for transesterification. The optimum operating conditions corresponding to 78.4%

yield of biodiesel production (FAME) using waste frying oil were found at reaction temperature 90°C, 3wt% montmorillonite clay K-30 catalyst loading, 1:12 molar ratio of oil to methanol, and 180 min of reaction time.

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